Coastal cryogenic processes and carbonate balance of the coastal waters of eastern Arctic seas in the light of a changing climate

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ABSTRACT: An observed increase in alkalinity of the East Siberian Sea during the last quarter of the XX century is the result of CO_2 absorption from the atmosphere, a more intense transport of organic substances into the water due to more active erosion of ice-rich coasts related to climate warming. Destructive coastal cryogenic processes disturb the carbonate balance causing sharp rises in a partial pressure of CO_2 up to $8 \cdot 10^{-4}$ in inshore waters and violations of the regular relative proportions of the alkali reserve and chlorine content. However, during summer seasons, a dominating partial pressure of CO_2 is much lower in waters than in the atmosphere and varies from $0.83 \cdot 10^{-4}$ to $1.89 \cdot 10^{-4}$ depending on physical and chemical conditions. The current climate changes have not yet affected a potential ability of the sea to absorb CO_2 from the atmosphere. On the other hand, a more active erosion of the ice-rich coasts due to climate warming reduces the ability of the sea to absorb CO_2, especially in coastal, cryogenically active sections of the water area.

1 INTRODUCTION

It is supposed that the concentration of CO_2 in the atmosphere depends on the ability of the ocean to absorb a surplus of the gas accumulating on behalf of climate warming. The Arctic Ocean and its seas with low-temperature water masses and actively eroded ice-rich shores play an important role in regulating the level of CO_2 concentrations in the atmosphere of the Northern Hemisphere.

A potential ability of the ocean to absorb CO_2 depends on the carbonate balance of the water masses. Relative proportions of the carbonate system components determine the pH of the water and hence its buffer properties and affect redox reactions in particular and ecological conditions of the Arctic seas in general. Coastal cryogenic processes substantially influence the formation of the carbonate balance. The study of the influence they have on the carbonate system of the seas gains a special importance with regard to climate changes. The latter are accompanied by variations of the water temperature, ice conditions, erosion rate of ice-rich coasts, and quantities of mineral and organic substances transported into the sea. All these factors directly influence the carbonate system. However, our knowledge in this field of geocryology is still quite insufficient.

2 COASTAL DYNAMICS UNDER CHANGING CLIMATIC CONDITIONS

The rate of retreat of thermoabrasion coasts of the Arctic seas changes widely in space and time depending on variations in summer air temperatures, ice conditions, the occurrence and duration of storms. To study the effect these climatic characteristics have on the dynamics of ice-rich coasts, observations were made at the following key sites of the Laptev Sea and East Siberian Sea coast: Anabar-Olenek shore, Bykovsky Peninsula, Muostakh Island, southern coast of Dmitry Laptev Strait, Cape Krestovsky and Cape Small Chukochy.

A relative fall in temperatures from the early 1950s to mid-1970s in the eastern Arctic Region was characterized by shorter ice-free periods, less areas of open water and less stormy winds from the east. In the above key sites, the rate of erosion of 0.7 m to 40 m high coasts exposed to the north and east was 0.6 m to 3.2 m/year and averaged 1.7 m/year (Semenov 1962, Kluev 1970, Are 1985). On Cape Krestovsky on the East Siberian Sea, in the shallow water from the shore line to 4 m to 5 m depth, sediments were washed out at a speed of 0.6 cm to 3.3 cm/year (average 1.4 cm/year). Within the 5 m to 7 m submarine contours, the speed of sedimentation was 1 cm to 3 cm/year (Razumov 2000b). On the Anabar-Olenek shore of the Laptev Sea, at depths of 1 m to 10 m, the speed of sedimentation reached 4–5 cm/year (Are et al. 2001).

A relative rise in temperatures in the Arctic region during the last quarter of the XX century was related to more intense air circulation accompanied by an increase of average summer air temperatures and ice-free areas in summers as well as by longer ice-free periods and storms. For example, on the southern coasts of the East Siberian Sea, the sum of air temperatures above zero increased from 132.7°C to 515.6°C over the period from the early 1960s to the 1990s, which accounted for an increase of the average summer temperature by 2.8°C [Razumov 2001]. The occurrence of

the storms increased by 3% to 4% (Fig. 1). During ice-free seasons, the total duration of the active influence of the water masses on the coastal permafrost soils increased from 58 hours to 100 hours on the average (Razumov 2000).

Due to the growth of the hydrodynamic activity of the seas and an increase in summer air temperatures, the erosion rate of 4 m to 30 m high ice-rich coasts in the key sites increased up to 3 m/year to 8 m/year and averaged 5.6 m/year (Fartyshev 1993, Grigoriev 1993, Grigoriev et al. 2001, Are et al. 2000, Razumov 2000a). Average erosion rates of 0.7 m to 2 m high coasts on Cape Krestovsky reached 10 m/year (Fig. 2). In the early 1990s, the erosion of the coast reached 13 m to 17 m/year in some places of the area (Razumov 2000, 2001). In the key sites, the erosion of the seabed reached 5 cm to 6 cm/year and averaged 2.6 cm to 3.5 cm/year (Razumov 2000b, Are et al. 2001).

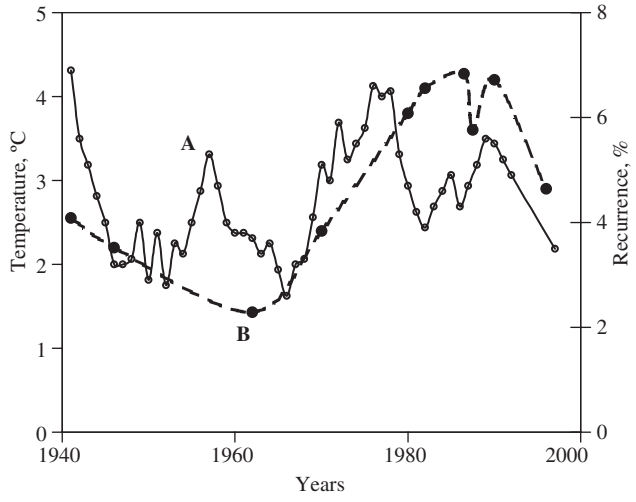

Figure 1. Changes in recurrence of stormy winds (A) and average summer air temperatures (B) in southern coastal areas of the East Siberian Sea.

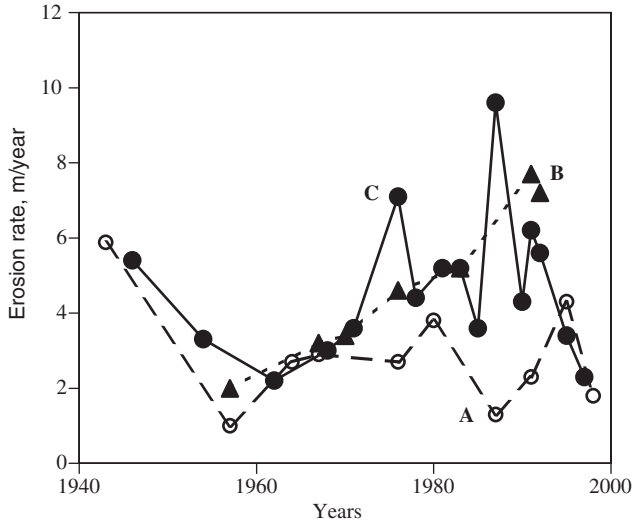

Figure 2. Changes in the average erosion rate of ice-rich coasts in key areas along the Laptev Sea (A – Bykovsky Peninsula, B – Muostakh Island) and East Siberian Sea (C – Cape Krestovsky).

3 CHANGE IN THE ALKALI RESERVE OF THE EAST SIBERIAN SEA

H.U. Sverdrup first studied the chemistry of waters of the area under consideration in 1918 to 1925 during the Maud expedition. In 1953 and 1954, hydrochemical studies were conducted by the AARI (Musina 1960, Musina & Avdeevich 1960). Recent investigations in the chemistry of the waters (32 samples from a square N 68° 20′ – 72° 00′, E 160° 00′ – 165° 00′) was made in 1987, 1990 and 1992 by the author during marine expeditions organized by the "Yakutsk geologia production association" and the Permafrost Institute. Alkalinity was measured using direct titration methods.

The analytical results show that carbonate alkalinity of the East Siberian Sea underwent almost no changes during the summers for a period from the early 1920s to early 1950s. However, it increased on the average by 0.21 mg · equivalent/liter at the end of the 1980s to early 1990s. In the southern part of the area, the alkalinity of the coastal waters having a temperature of 2°C to 12°C, pH of 7.0 to 7.9 and salinity of 1.6‰ to 25‰ increased to 0.25 to 0.4 mg · equivalent/liter (Fig. 3).

The changes in the carbonate balance resulted primarily from absorption by the sea over several decades as part of the excessive CO_2 accumulated in the atmosphere during global climatic warming, as well as from intense transport of organic substances into the water area due to active erosion of the ice-rich coasts. Parts of the carbon dioxide, absorbed from the

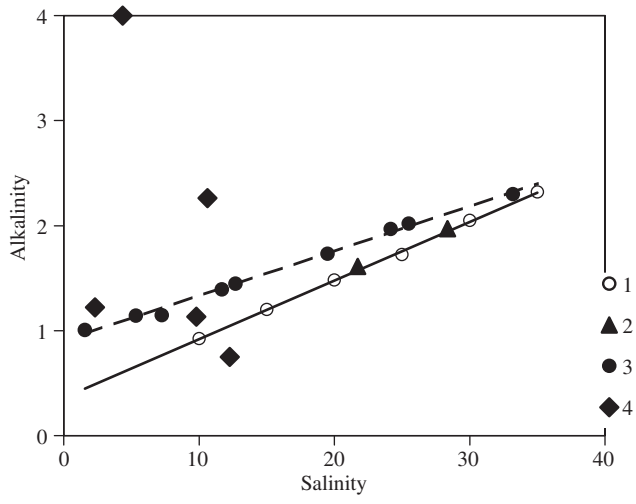

Figure 3. Alkalinity of the Siberian Sea water at different salinities and different years: 1 – 1918–1925; 2 – 1953, 1954; 3 and 4 – 1987–1992: 3 – seaward from the coast; 4 – in coastal cryogenically active areas.

atmosphere and released from oxidized organic matter, is consumed by the formation of carbon dioxide and to dissolve calcium carbonate carried into the water area with coastal erosion and river load. As a result, the carbonate balance of the waters is shifted towards an increased alkalinity.

Free carbon dioxide increases the partial pressure of CO_2 in the water. However, under the hydrometeorological conditions of summer periods, with moderate winds and (calms) calm spells, no gas release into the atmosphere occurs. Our calculations using the methods described by Konovalov et al. 1989 show that partial pressure of CO_2 in coastal waters with the above characteristics varies between $0.83 \cdot 10^{-4}$ and $1.89 \cdot 10^{-4}$. These values are much lower compared to the partial pressure of CO_2 in the atmosphere, e.g. about $3.1 \cdot 10^{-4}$ in the higher latitudes (Horne 1969).

An exception is the fore delta of the Kolyma River where muddy river and transparent sea waters meet. There, at temperatures of 4°C to 7°C and salinity 13‰ to 20‰, a partial pressure of CO_2 in the water increases up to $3.2 \cdot 10^{-4}$ to $6.1 \cdot 10^{-4}$ as a result of intense oxidation of organic substances. Under such conditions, the carbon dioxide is released into the atmosphere.

The alkalinity is also affected by the inflow of dissolved carbonates into the sea. By our estimation, 10.9 million tons of dissolved carbonates and about 55 thousand tons of solid carbonates flow each year into the Eastern Siberian Sea with a suspension load of the streams and erosion of the ice-rich coasts.

Coastal sediments of ice complexes and alasses on the average contain 0.07% of tiff (34 samples). The average content of dissolved carbonates in a water volume of 60.7 thousand km^3 should increase within 35 years by 6.3 mg/l taking into account tiff dissolution, which would correspond to an increase in the alkali reserve by 0.1 mg · equivalent/liter. As can be seen, such an increase of the alkali reserve due to carbonate inflow with river load and coastal erosion is substantially less than the one actually observed.

Thus, no carbon dioxide is released from the seawater into the atmosphere with a climate warming because for most of a thawing season its partial pressure in the water is much lower compared to that in the air. Summers are dominated by CO_2 invasion from the atmosphere, which is evidenced by an increased alkali reserve and insignificant saturation of coastal waters with calcium carbonate. The saturation coefficient varies from 0.07 m to 0.77 in the upper water horizons up to 1.56 near the seabed.

No supersaturation and chemical precipitation of calcium carbonate is observed in the East Siberian Sea. Coastal sediments at depths of 5 m to 7 m have very low calcite concentrations, averaging from 0.025% in September to 0.2% in July–August (11 samples). Most probably, calcite accumulation from clastic materials of eroded coasts is gradually dissolved because shelf sediments at water depths exceeding 7 m (72 samples) do not contain any calcite at all.

4 CARBONATE BALANCE DYNAMICS OF THE WATERS OF CRYOGENICALLY ACTIVE AREAS

Destructive coastal cryogenic processes under changing climatic conditions cause substantial variations in physical and chemical properties and, hence, disturb the carbonate balance of the coastal waters. The balance of the carbonate system is easily disturbed by decomposition of organic substances transported in large quantities into the sea through active erosion of the ice-rich coasts. By our estimate, the annual influx of organic matter into the East Siberian Sea is approximately 3 million tons, assuming the average organic carbon content of the ice complex and alass sediments to be 4% (Schirrmeister et al. 2002).

In cryogenically active areas (for example, the coast west of the Kolyma River mouth), water alkalinity in summer depends on hydrodynamic conditions and changes from 0.749 to 4.021 mg · equivalent/liter with salinity variations from 2.3‰ to 12.3‰ (see Fig. 3). During a storm event from 12th to 14th August 1990 in the area of Cape Krestovsky, accompanied by active erosion of ice-rich coasts, the alkalinity of the coastal waters with temperatures of 5°C to 6°C and a salinity of 12‰ to 13‰ was 0.749 mg · equivalent/liter. The NH_4^+ content of the waters reached 1 mg/liter. Intense oxidation of the organic substances that came into the water area with the eroded material, had led to a strong increase in the partial pressure of CO_2 in coastal waters and its release into the atmosphere. Under such conditions we estimated the free CO_2 content of the water to be 20.4 mg/liter with a pressure of $8.1 \cdot 10^{-4}$.

A decrease in the alkali reserve with a strong inflow of carbonates and organic matter into the sea may be related to the presence of nitrogen bearing salts. The pH and calcium carbonate saturation coefficient of the water samples taken during the storm were 6.6 and 0.03, respectively. These values evidence that carbonates, in fact, completely dissolve in CO_2 saturated water. No calcium carbonate was found in submarine slope sediments after the storm.

Summers are dominated by moderate winds and calm spells. In the upper layer of coastal waters of the sea, the temperature ranges between 4°C and 12°C, the salinity between 2.3‰ and 11.7‰, the alkalinity between 1.131 and 1.392 mg · equivalent/liter, the pH between 7.5 and 7.9, CO_2 the partial pressure between $0.89 \cdot 10^{-4}$ and $1.64 \cdot 10^{-4}$. The saturation coefficient of $CaCO_3$ does not exceed 0.77. A relatively high

alkalinity – 2.794 mg · equivalent/liter – was measured for the bottom layer of the water at of depth of 5 m, with a temperature of 2.8°C, a pH of 8.0 and a salinity of 11‰. The saturation coefficient of calcium carbonate was 1.56 and the CO_2 pressure $0.95 \cdot 10^{-4}$.

The increase in alkalinity near the seabed appears to be related to active transformation of the carbon dioxide liberated from oxidized organic matter of the seabed sediments, into bicarbonates. With a decrease of the carbon dioxide concentrations, a small part of bicarbonates grades into carbonates. Dissolved calcium carbonate somewhat increases in concentration in the bottom layer, but chemical precipitation of tiff does not occur owing to weak saturation of water with calcium carbonate.

Estimates of the partial pressure of CO_2 in the water are lower than in the atmosphere. Therefore, in the given hydrometeorological conditions, an invasion of CO_2 from the atmosphere is most probable.

A maximum alkalinity of coastal waters (4.021 mg · equivalent/liter) was fixed in September 1992 with moderate waves, temperatures between 0°C and 1°C, a pH 7.5, and a salinity 4.4‰. The partial pressure of CO_2 in water was $5.81 \cdot 10^{-4}$, the calcium carbonate saturation coefficient 0.65. Under such conditions, the inshore waters of the considered area may release carbon dioxide into the atmosphere, notwithstanding a higher solubility of the gas in colder temperatures.

The reason for this maximum value of alkalinity is difficult to define so far. It could be intense dissolution of biogenic tiff predominantly as bicarbonates, with a high CO_2 saturation of water at relatively low temperatures. The calcium carbonate could have been transported into the sea with suspension load of the streams that eroded tiff-enriched areas of low coastal terraces, or with moderate erosion of beaches that locally contained accumulations of mollusk shell fragments. According to our data, the tiff content of the light and heavy fractions of concentrates reach 80.6% and 94%, respectively there.

5 CONCLUSIONS

During climate warming in the Arctic between the 1970s to 1990s, the alkali reserve of the East Siberian Sea waters increased by 0.2–0.4 mg · equivalent/liter in comparison with the time of relatively cold spell at the beginning and in the middle of the XX century. The main reasons for the changes in the carbonate balance were absorption by the sea during several decades when parts of the excess CO_2 accumulated into the atmosphere during global climate warming, as well as an intense inflow of organic matter into the sea due to active erosion of the ice-rich coasts. Nonetheless, overall partial pressure of carbon dioxide remains lower in the water than in the atmosphere.

Upon relative warming of a climate, the time of direct influence of the sea on the coasts took approximately two times longer compared to cold spells. The erosion rate of ice-rich coasts increased three to six times, whereas that of underwater slope sediments only two to three times.

The climatic changes have a strong influence on the carbonate balance of the inshore waters due to active erosion of ice-rich coasts enriched in organic substances. A considerable destabilization of the carbonate balance is marked in cryogenically active sites of the water area. In summers, the range in variation of the inshore water alkalinity is 0.749 to 4.021 mg · equivalent/liter, pH 6.6 to 8.0, CO_2 partial pressure $0.83 \cdot 10^{-4}$ to $8.1 \cdot 10^{-4}$, calcium carbonate saturation coefficient 0.03 to 1.56. The maximum partial pressure of CO_2 in the water being substantially higher than in the atmosphere was observed under storm conditions, with an active destruction of ice-rich coasts. Releases of the gas into the atmosphere obviously take place under such conditions.

Under the existing climatic conditions, the sea is in general retaining its potential ability to absorb carbon dioxide from the atmosphere, notwithstanding an intense inflow of organic matter. At the same time, by destabilizing the carbonate balance, the active erosion of ice-rich coasts decreases the sea potential to absorb CO_2 from the atmosphere, especially in cryogenically active areas of the sea.

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